ORGANIC CONDUCTORS
AS NANORULERS AND TEMPLATES FOR NANOFABRICATION

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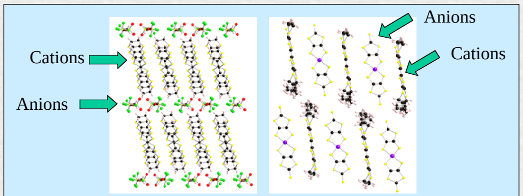
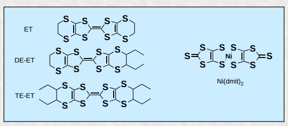
Layered molecular conductors, in which cationic organic layers *alternate* with anionic layers, are a widely studied class of materials because of a rich variety of electronic and magnetic properties that they exhibit. Reduced dimensionality and electron correlation effects in these materials also make them an ideal reference point for gaining important insights into high-T_c superconductivity. On the other hand, when the cationic and the anionic components are *similar in size and structure*, both these components pack in the *same* layer, which repeats itself giving rise to another type of layered structure.



Two examples of layered structures

Examples of the latter materials include cation-radical salts of the organic electron donor molecule BEDT-TTF (or ET) with $[Ni(dmit)_2]^-$ anions (see below, left panel), which can be grown as large, plate-like crystals (see below, right panel). Furthermore, by appending substituents (e.g., ethyl groups) on the ET skeleton, we have shown earlier that it is possible to modulate the lattice parameters in these crystals.



The crystal structure and molecular packing in these crystals are depicted below.

(ET)[Ni(dmit)$_2$]
a =7.355 b =6.667 c =15.031Å

(DE-ET)[Ni(dmit)$_2$]$_2$
a =7.639 b =10.147 c =31.019Å

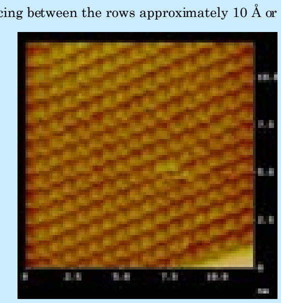
(TE-ET)[Ni(dmit)$_2$]$_2$
a =7.509 b =10.199 c =17.097Å

Some intrinsic and characteristic features of the crystals

- Highly stable in both air and vacuum
- No surface reconstruction
- Large and tunable periodicities of >10Å
- Sufficiently conducting to obtain STM images

STM images of (TE-ET)[Ni(dmit)$_2$]$_2$ reveal

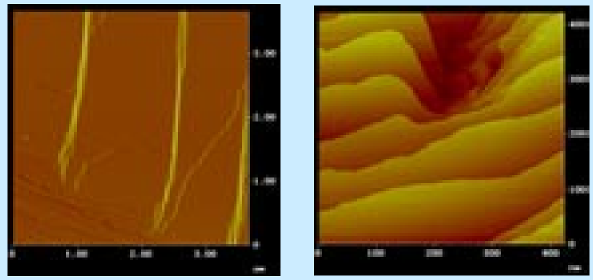
- Periodic arrays of component molecules arranged in rows
- Spacing between the rows approximately 10 Å or 1 nm

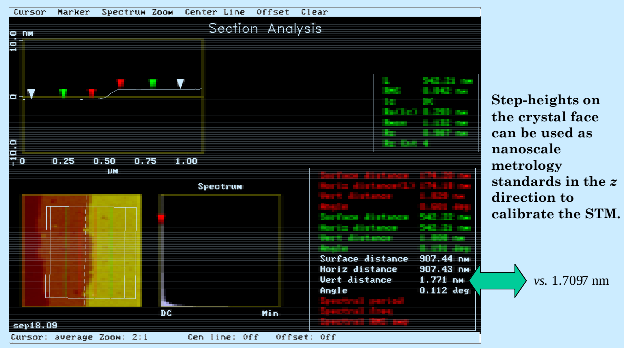


Since the spacing between the rows is known precisely from the x-ray structural data to be 1.020 nm or 10.20 Å (traceable to x-ray wavelength λ=0.71069Å), crystal surface can be used as a nanoscale metrology standard in *x* and *y* directions to calibrate the STM.

AFM images of (TE-ET)[Ni(dmit)$_2$]$_2$ crystals reveal

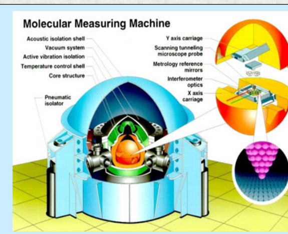
- Micron-scale mesas and terraced steps on the crystal surface
- Step-heights correspond to one lattice spacing (17.097 Å)



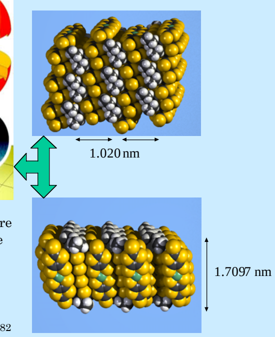


Step-heights on the crystal face can be used as nanoscale metrology standards in the *z* direction to calibrate the STM.

The molecular conductor crystals developed here, *because of their intrinsic conductivity, plate-like morphology, stability and nanometer-scale structural periodicity*, are uniquely suited to be used as dimensional metrology standards on the nanometer length scale in *x*, *y* and *z* directions, especially in metrology tools utilizing STM. The "molecular ruler" crystals are currently being used in the "Molecular Measuring Machine" at NIST (see below), and are being developed as a "Standard Reference Material (SRM)" to satisfy the future metrology demands of the semiconductor chip manufacturing industry as the chip feature sizes shrink to a few nanometers.



M³ at NIST, the lead agency to develop future metrology tools and standards as part of the "SEMATECH Metrology Roadmap".



(TE-ET)[Ni(dmit)$_2$]$_2$ crystal as a Standard Reference Material (SRM)
http://ois.nist.gov/srmcatalog/FY00SRMProject.htm#Devel82

Templates for Nanofabrication: (TE-ET)[Ni(dmit)$_2$]$_2$ crystals, on their largest crystal faces, have highly regular arrays of sulfur atoms and hydrophobic alkyl groups, which have vastly different chemical affinities to transition metals (Fe, Cr, Ni, Cu etc.) and noble metals (Ag, Au, Pd, Pt etc.). These arrays are typically *ca.* 1 nm apart, and this distance can be systematically varied by varying the sizes of the molecular components. Deposition of the aforementioned metals on these crystal surfaces is expected to lead to selective deposition on the sulfur atom arrays and not on the alkyl group arrays. Nanowires of single digit nm dimensions can be fabricated by the conventional MBE thin film deposition technique. (In collaboration with D. Li & S. Bader, Nanomagnetism, FWP 58830)

SUMMARY

- "Molecular Ruler" crystals, which combine intrinsic conductivity, plate-like morphology, ambient and vacuum stability, and nanometer-scale structural periodicity in the *same* material, have been developed.
- These crystals have been found to be superior dimensional metrology standards on the nanometer scale in *x*, *y* and *z* directions, especially in metrology tools utilizing STM.
- These crystals are also anticipated to be good templating substrates for the fabrication of nanowires of single digit nm dimensions.

Supported by DOE, BES-Materials Science under contract W-31-109-ENG-38

Molecular Materials, FWP 58510